Microstructure imaging and electrolyte transport property measurements for mathematical modeling
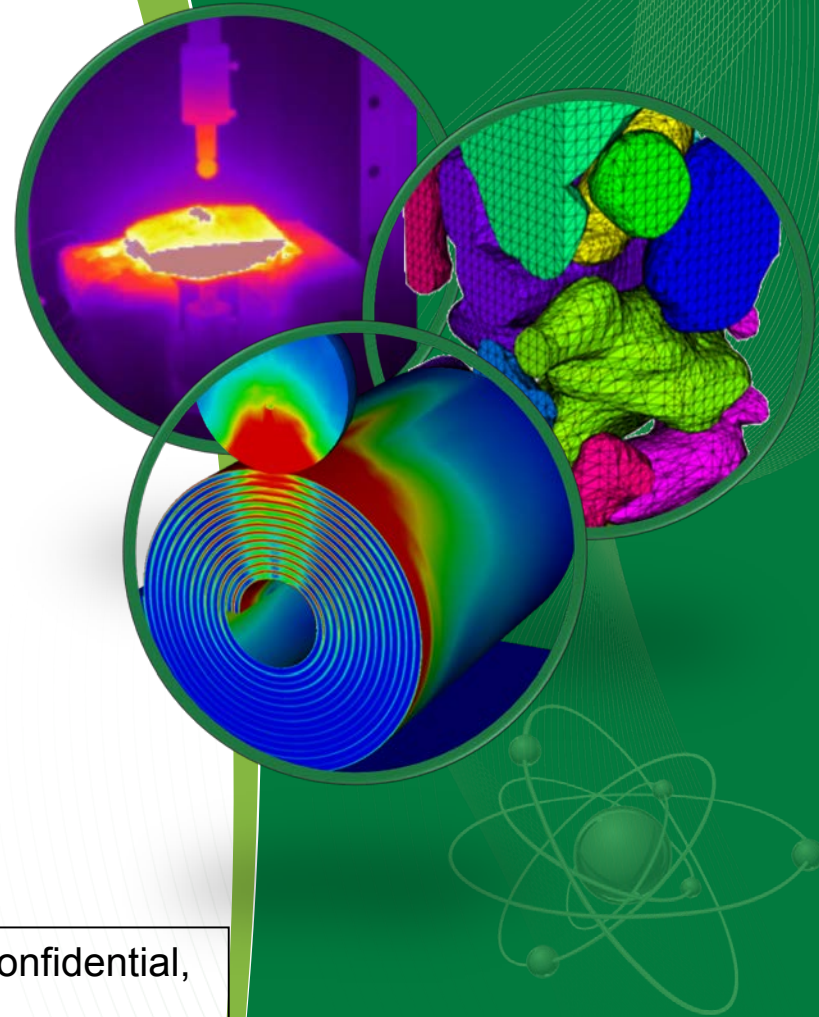
Venkat Srinivasan

Team: CABS

2017 U.S. DOE Vehicle Technologies Office Annual Merit Review

June 6, 2017   **Project ID:** ES302

CABS **C**onsortium for **A**dvanced **B**attery **S**imulation

OAK RIDGE National Laboratory | Argonne NATIONAL LABORATORY | BERKELEY LAB | Sandia National Laboratories

Overview

Timeline

- Project start date: October 2015
- Project end date: September 2018
- Percent complete: 58%

Barriers Addressed

- High cost
- Low performance

Budget

- FY 16
    - Total CABS funding: 2265K
    - This effort: 620K
- FY 17:
    - Total CABS funding: 2225K
    - This effort: 630K

Partners

- Vince Battaglia
- Gao Liu
- CD-Adapco/Siemens
- Advanced Light Source (Dula Parkinson)
- Advanced Photon Source (Xianghui Xiao)

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Relevance

Objective: Provide accurate simulation input data for CAEBAT teams, enabling construction of accurate models to guide cost and performance optimizations

- Obtain electrode microstructure data and generate surface meshes for simulation domains
  - Collect data under realistic conditions
    - Compressed
    - Immersed in solution
    - Pristine and cycled

- Obtain concentration-dependent electrolyte transport property measurements
  - Use non-electrochemical approaches
  - Pulsed field gradient NMR
  - Diffusion in microfluidic channel

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Milestones

• Produce segmented tomographic reconstructions of electrodes for conversion to spatial domains for microstructural models (June 2016)

Completed

• Obtain concentration-dependent transport properties in electrolyte solution (March 2017)

Completed

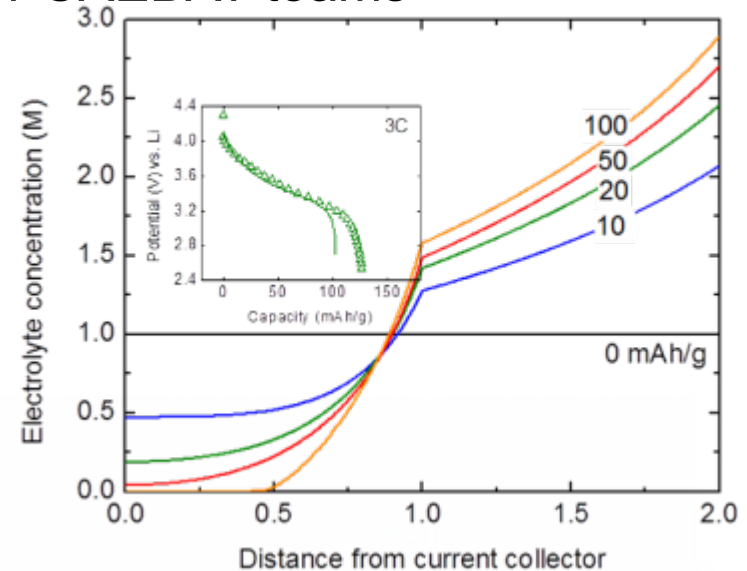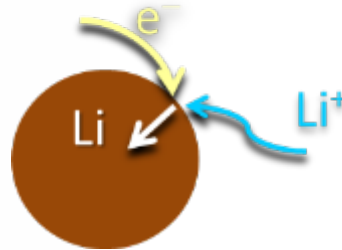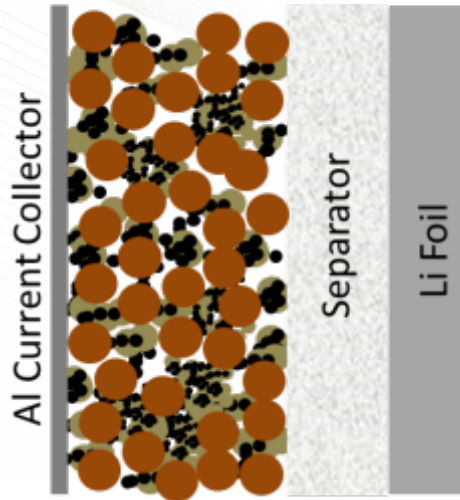• Obtain electrode image data from cycled electrode material (December 2017)

In Progress

Sept 2015

Sept 2016

Sept 2017

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Argonne NATIONAL LABORATORY

BERKELEY LAB

Sandia National Laboratories

Approach

- Provide accurate simulation input data for CAEBAT teams

- Accurate electrode microstructure and solution transport properties are critical for accurate battery simulations
  - Affect ionic transport, determine battery performance limitations

- Experimental approaches
  - X-ray microtomography for imaging of electrodes under realistic conditions
  - Non-electrochemical measurements of transport properties

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Technical Accomplishments and Progress: X-ray microtomography of electrodes

Custom sample holders mimicking real battery environment
   Samples immersed in electrolyte solution, under light pressure

- Multiple samples per reusable sample holder to increase throughput and consistency of results

- Samples imaged at ALS BL8.3.2 (Dula Parkinson) and APS 2-BM-A (Xianghui Xiao)

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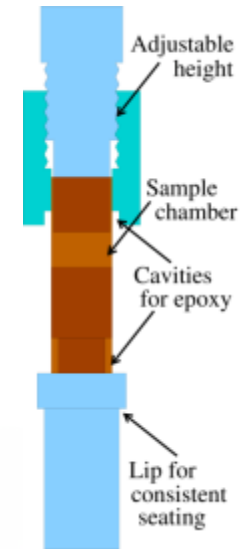
Tomography reconstructions to surface meshes

- Cylindrical electrode regions reconstructed from transmission images

- Voxel intensities describe X-ray absorption by material in small spatial regions

- Processing pipeline incorporating custom programs, ImageJ, Avizo (script modified from SNL) produces particle surface meshes

1.6384 mm

115.1 microns

115.1 microns

**CABS** Consortium for Advanced Battery Simulation
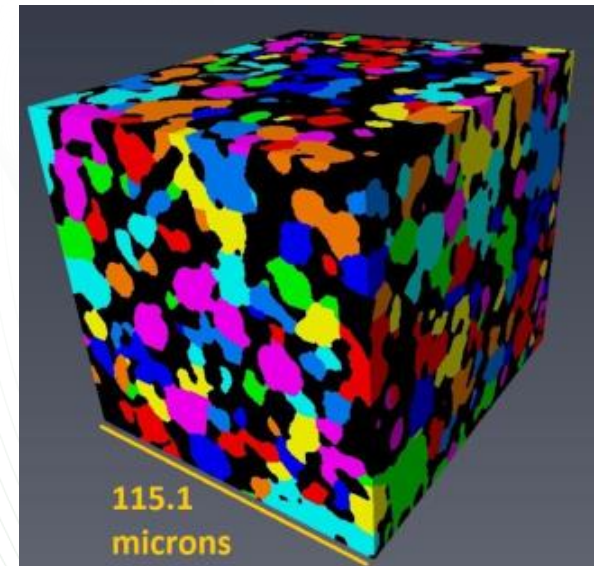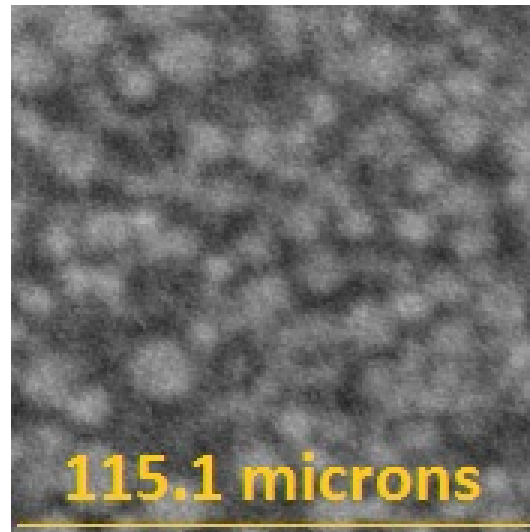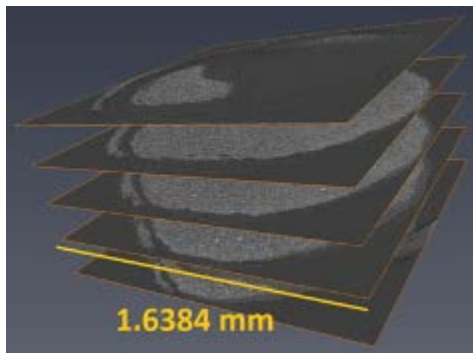
Effect of wetting and pressure

- Unquantified light pressure on dry samples and samples wetted with electrolyte solution

- Wide variation in wet sample thickness

- Kitchen sponge analogy: rigid when dry, easily compressible when wet even though material swells with solution
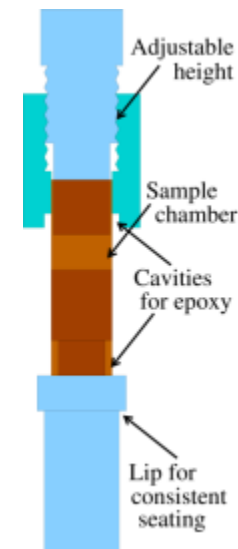
Potentially significant (about 20%) reduction in thickness from dry state
   Significant implications for models and experiments
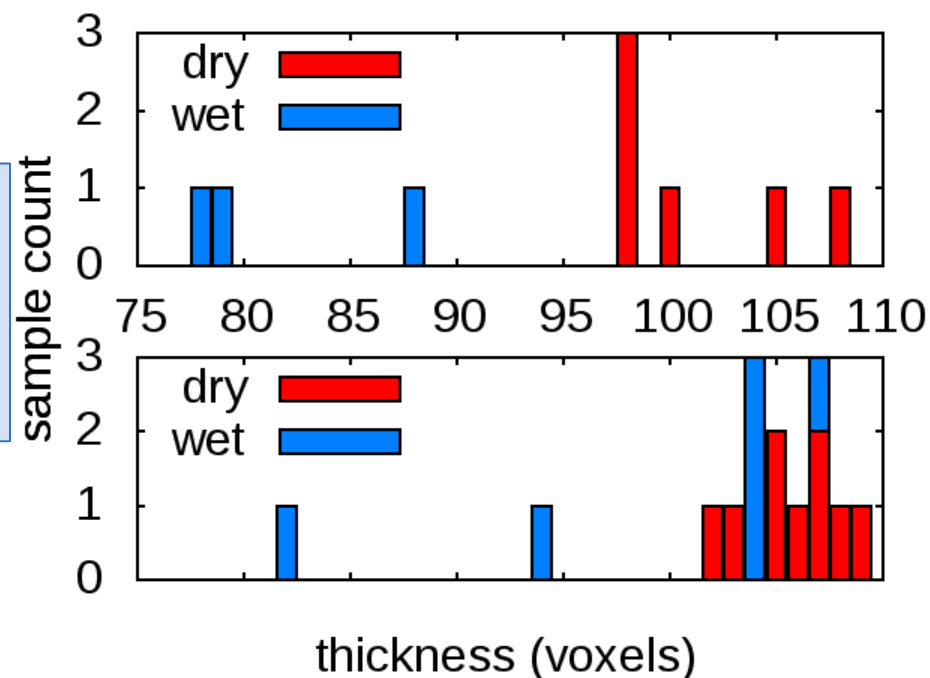
Effect of epoxy impregnation

- Popular sample preparation procedure for imaging

- Electrode material (Sergiy Kalnaus, ORNL) impregnated with optical epoxy (Tom Johnson, LBNL)
  - Low viscosity, no filler, minimal volume change

- Was microstructure affected?
  - Have particles moved? Did electrode thickness change?
  - Analysis in progress

Technical Accomplishments and Progress: Electrolyte transport property measurements

- Possible concerns with electrochemical methods:
  - Potential drift of Li metal
  - Side reactions on Li electrode
  - Convection in electrochemical cells
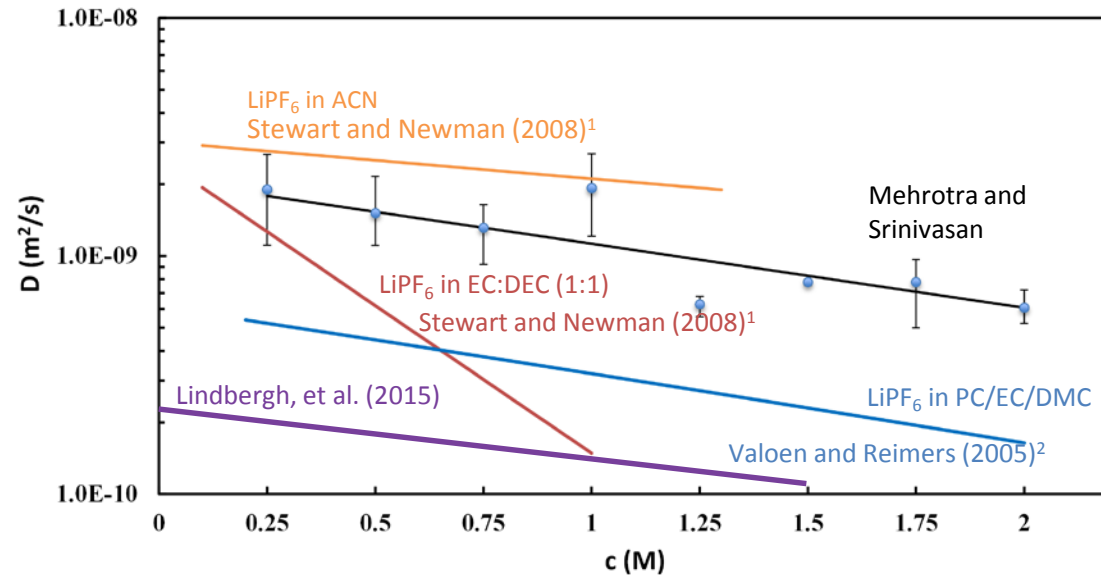
- Diffusivity
- Transference number
- Conductivity
- Degree of dissociation

- Various concentrations of $LiPF_6$ in mixture of EC/DEC (1:1 by weight)

Pulsed Field Gradient-NMR Spectroscopy[1]

- Easy to remove effect of convection

- Measures self-diffusivities of species with Li, F, H nuclei
  - PFG-NMR: radio-frequency pulses used to "label" nuclei of interest, according to position
  - Self-diffusivities: diffusion coefficients of species in absence of concentration gradient
  - Can distinguish between EC and DEC from chemical shifts

- In the literature, analysis has been conducted assuming dilute limits
  - Not applicable for typical electrolytes where interactions are stronger.

Further, ion-pairing analysis needed for $LiPF_6$, Li^+, PF_6^-

1. Stejskal and Tanner, J. Chem. Phys. 1965, 42(1), 288-292

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Data suggest solvents can be combined
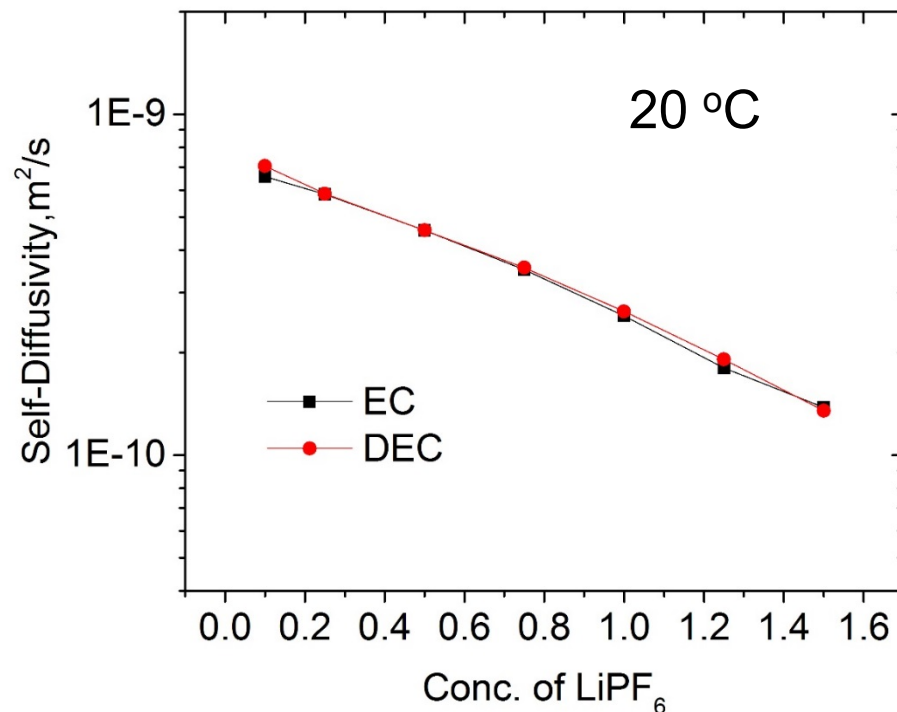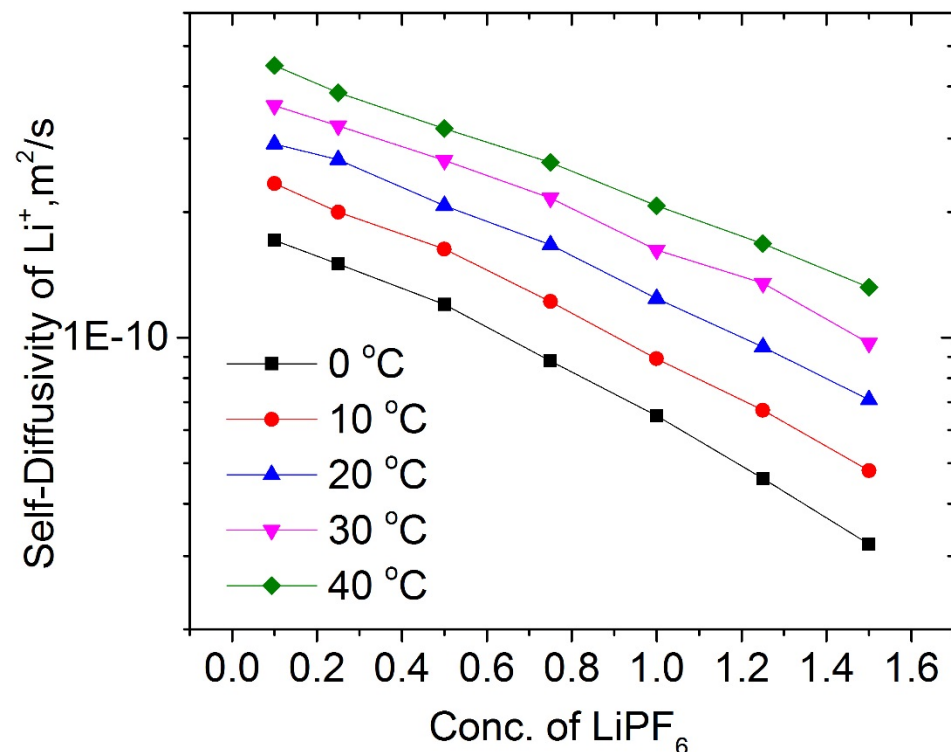
- Stokes-Einstein equation
  - Concentration increases viscosity
  - Self-diffusivities qualitatively reasonable

$$D = \frac{kT}{c\pi\eta r_s}$$

EC and DEC have similar self-diffusivities, will be treated as single "solvent" species in analysis

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From measurements to model parameters

Model parameters[1]

$$D = \mathcal{D} c_T \overline{V}_0 \left(1 + \frac{d \ln f_{+-}}{d \ln c} \right)$$

$$\mathcal{D} = \frac{(z_+ - z_-)\mathcal{D}_{0+}\mathcal{D}_{0-}}{z_+\mathcal{D}_{0+} - z_-\mathcal{D}_{0-}}$$

$$t_+^0 = \frac{z_+\mathcal{D}_{0+}}{z_+\mathcal{D}_{0+} - z_-\mathcal{D}_{0-}}$$

Generalized Darken Relation[2,3]

$$\mathcal{D}_{ij} = \frac{x_i}{x_i + x_j}\hat{D}_j + \frac{x_j}{x_i + x_j}\hat{D}_i.$$

Ind. Eng. Chem. Res. **2005**, *44*, 6939–6947   6939

The Darken Relation for Multicomponent Diffusion in Liquid Mixtures of Linear Alkanes: An Investigation Using Molecular Dynamics (MD) Simulations

R. Krishna* and J. M. van Baten

Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands
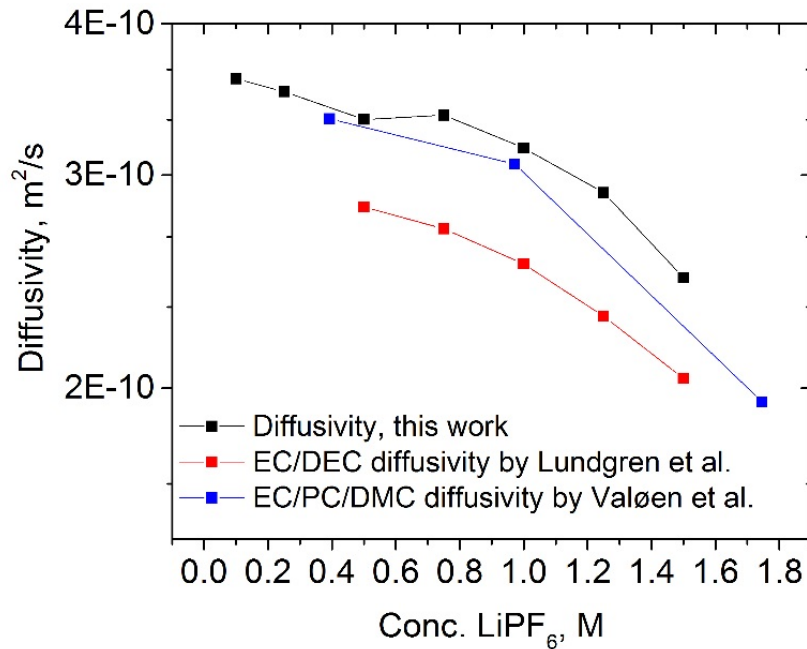
Molecular dynamics (MD) simulations have been performed for binary, ternary, and quaternary liquid mixtures of linear alkanes containing 1−16 carbons. Both the self-diffusivities ($D_{i,\text{self}}$) and the Maxwell−Stefan (M−S) diffusivities ($\mathcal{D}_{ij}$) were determined from the MD simulations for various mixture compositions. The self-diffusivity was determined to be a linear function of the mass fractions ω_j of the constituent species in the mixture: $D_{i,\text{self}} = \sum_{j=1}^{j=n} \omega_j D_{i,\text{self}}^{x_j \to 1}$ where $D_{i,\text{self}}^{x_j \to 1}$ is the self-diffusivity of infinitely dilute species i in species j. The Maxwell−Stefan diffusivity of the binary $i−j$ pair in a multicomponent mixture was determined to be predicted reasonably well by the generalization of the Darken relation: $\mathcal{D}_{ij} = [x_i/(x_i + x_j)]D_{j,\text{self}} + [x_j/(x_i + x_j)]D_{i,\text{self}}$, where x_i is the mole fraction of species i.

## Self-diffusivities

D_{++}, D_{--}, D_{00}

1. J. S. Newman and K. E. Thomas-Alyea, *Electrochemical systems*, J. Wiley, Hoboken, N.J. (2004).
2. R. Krishna and J. M. van Baten, *Ind. Eng. Chem. Res.*, **44**, 6939 (2005)
3. S. U. Kim and V. Srinivasan, J. Electrochem. Soc., **163**, A2977 (2016)

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Properties consistent with literature

$$\frac{1}{\kappa} = \frac{-RT}{F^2 z_+ z_- c_{\mathrm{T}}} \left[\frac{1}{\mathcal{D}_{+-}} + \frac{c_0 t_-^0}{c_+ \mathcal{D}_{0-}} \right]$$

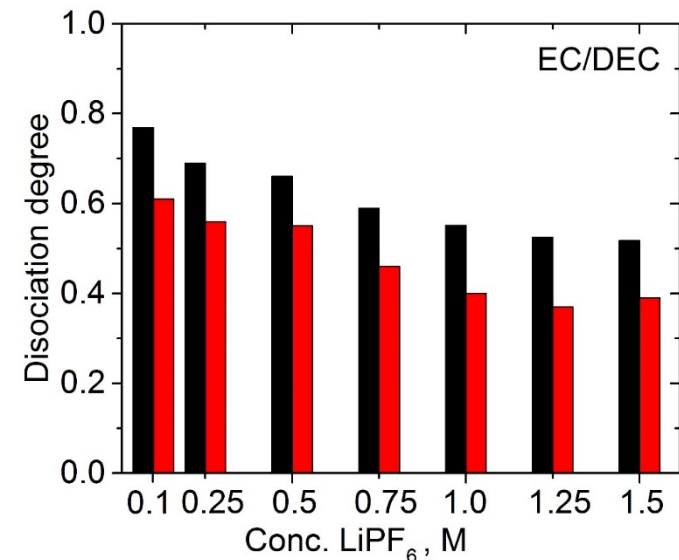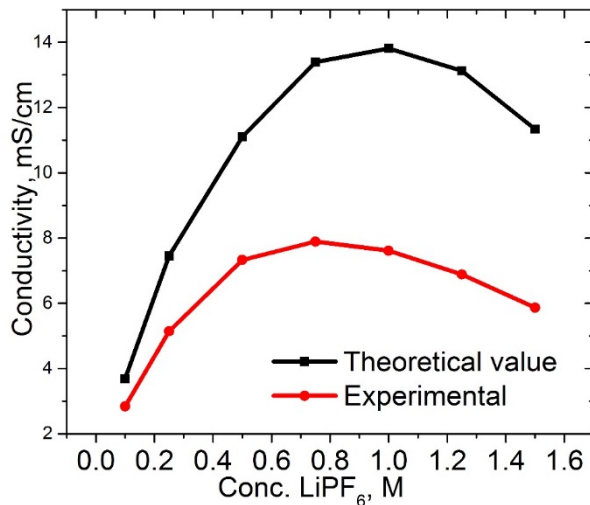Only dissociated ions carry current; discrepancy indicates ion-pairing.
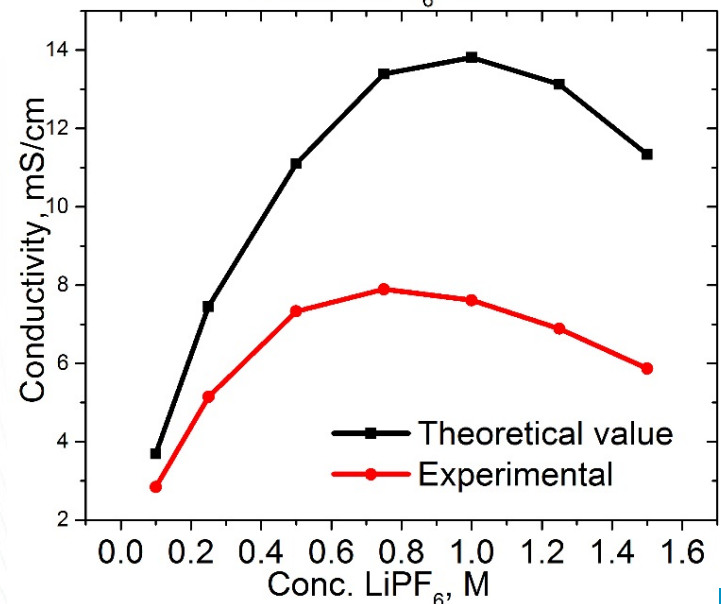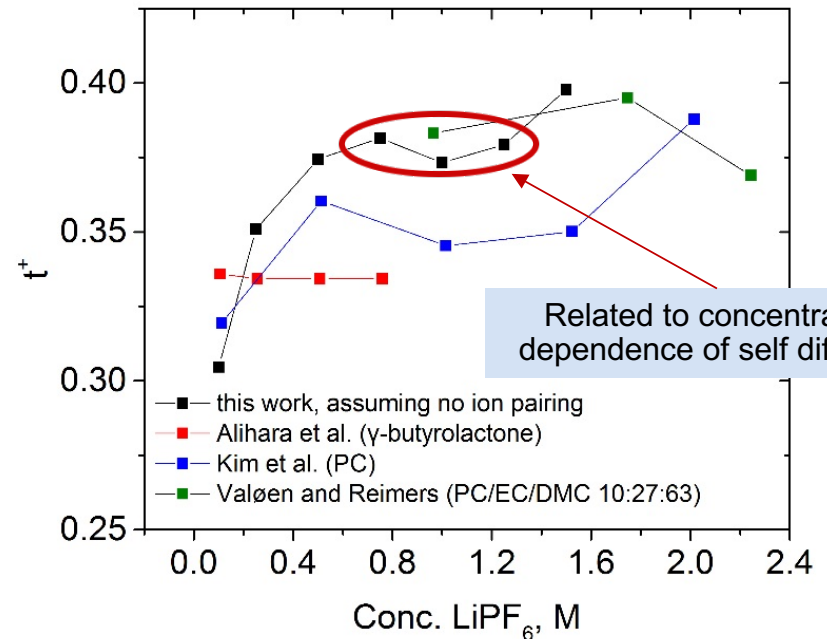
Use conductivity data to extract degree of dissociation

$$D_{++} = \frac{D^7{}_{Li} - (1-\alpha)D_p}{\alpha}$$

$$D_{--} = \frac{D^{19}{}_{F} - (1-\alpha)D_p}{\alpha}$$

α: dissociation degree
D_p: Diffusion of paired ion

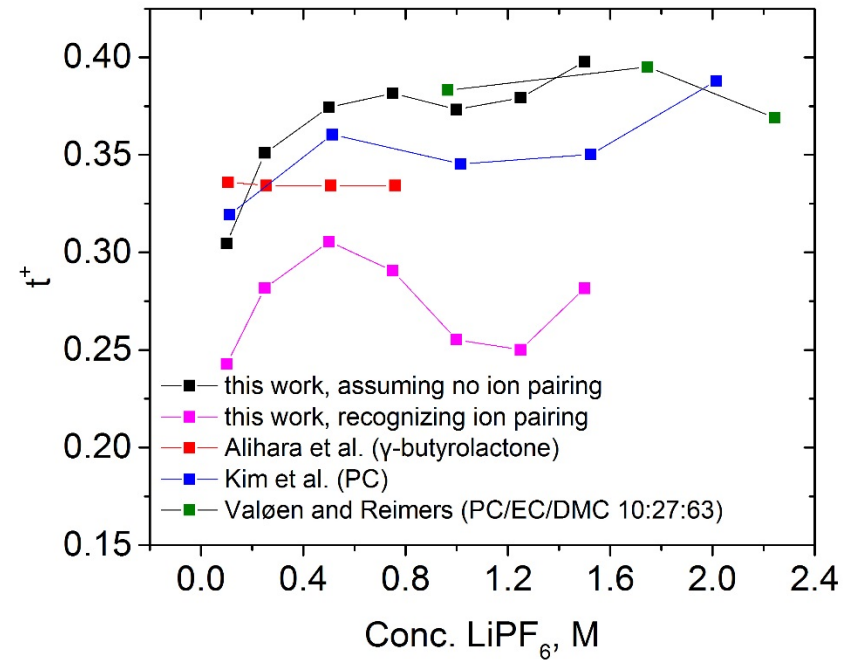Assuming $D_p = D_{++}$[1] allows extraction of α and correct D_{++} and D_{--}

Even in dilute solutions, ion pairs exist[1,2]

Black bars: Haven ratio
Red bars: Generalized Darken relation and Conc. Soln. theory

1. S. A. Krachkovskiy *et* al.,Electrochem. Soc., 164, A912, (2017)
2. C. M. Burba and R. Frech, J. Phys. Chem. B, 109, 15161 (2005).

Recalculated D and t⁺
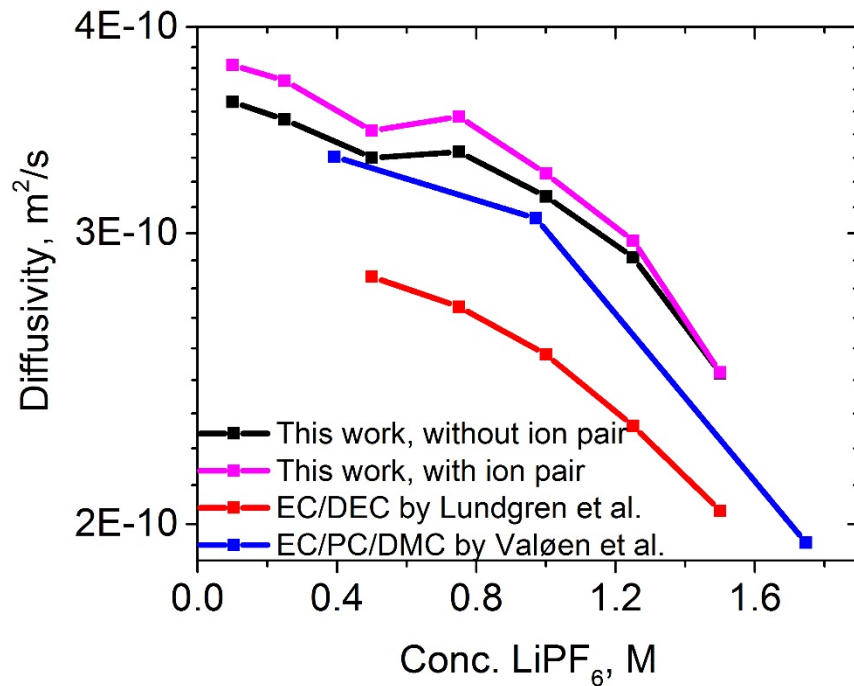
PFG-NMR method has many advantages:
- Allows extraction of all transport properties
- Can quantify degree of dissociation
- Simpler than electrochemical techniques

Technical Accomplishments and Progress: Microfludic evaluation of diffusivity

• Non-electrochemical method

• Minimizes vibration-induced convection

• Only salt diffusivity, not measurements for all species

  – Validation of PFG-NMR results

1
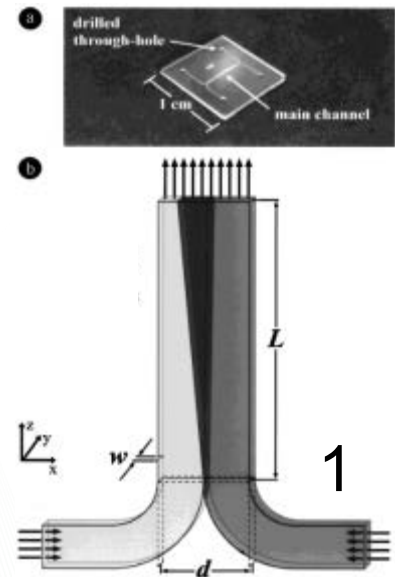
1. Kamholz, A. E., Weigl, B. H., Finlayson, B. A. & Yager, P. Quantitative analysis of molecular interaction in a microfluidic channel: The T-sensor. Analytical Chemistry 71, 5340-5347 (1999).
2. J. Forster, S. Harris, and J. Urban, J. Phys. Chem. Lett. 2014, 5, 2007−2011

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Combined model/experiment approach

- Diffusion between streams of different inlet concentration

- Concentrations of $LiPF_6$ in separate outlet streams characterized by ICP-OES

- COMSOL Multiphysics packages:
  - Laminar flow ($Re \approx 1$)
  - Fickian diffusion

Results approximately consistent with PFG-NMR
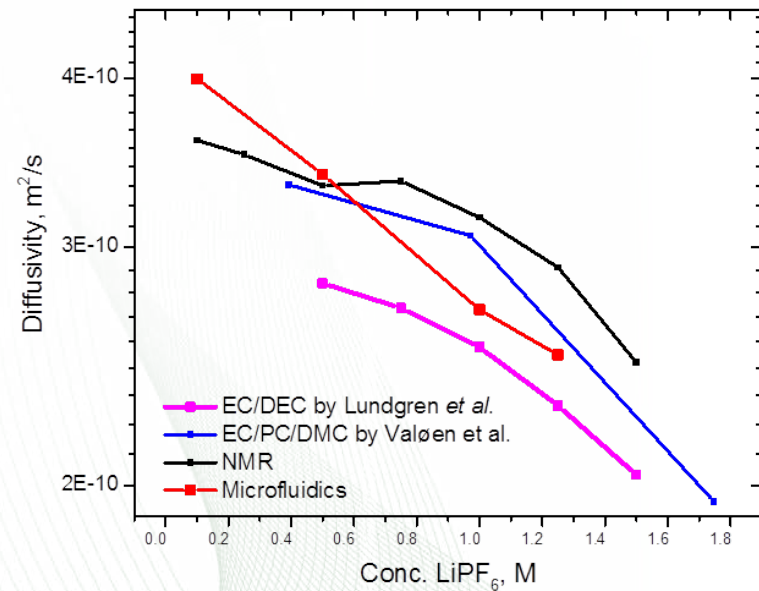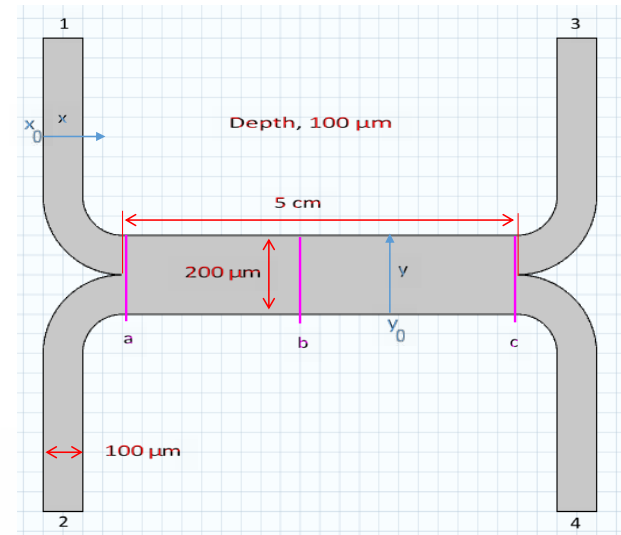
Responses to Previous Year Reviewers' Comments

- Reviewer 3 was unclear as to whether the tomographic work was carefully planned, and noted that the problem of representative volume size was not addressed.

    - The Srinivasan group had tested multiple iterations of sample holder designs and data pipelines prior to the start of this project. The present sample holder design has performed well, and the data processing pipeline is now nearly fully-automated.

    - The small (1/16" diameter) physical sample size was chosen to maximize X-ray imaging quality. The processing pipeline can provide voxel blocks of sizes up to the length scale of the physical sample size, but the identification of a representative size is left to the simulation efforts in the CABS program.

- Reviewer 3 suggested that accurate NMR measurements of diffusivity would be difficult due to ion-pairing. We have demonstrated the ability to separate ion-pair and solvated ion contributions to diffusivity with our methods, and have computed transport properties corrected for the degree of dissociation.

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Collaboration and Coordination with Other Institutions

- CD-Adapco
  - 3D simulation software

- DOE User Facilities (Outside VT Program)
  - Advanced Light Source (Dula Parkinson)
  - Advanced Photon Source (Xianghui Xiao)

- Within VT Program
  - Vince Battaglia
  - Gao Liu

Remaining Challenges and Barriers

- Microstructure imaging:
  - Need better resolved images with more accurate assignment of material identity
  - Reconstruction software bugs
  - Experiment design for imaging cycled electrodes (FY18 milestone)

- Transport property measurements
  - Need to modify analysis for EC/EMC 3:7 system

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Proposed Future Research

- Microstructure imaging
  - Currently processing lower-noise data from APS
    - Effect of epoxy impregnation (non-milestone)
  - Cycled electrodes (FY18 milestone), will test multiple *in situ* approaches as well as extraction from cells

- Transport property measurements
  - $LiPF_6$ in EC/EMC 3:7 (non-milestone)
  - Macro-homogeneous battery model incorporating corrections for ion-pairing (non-milestone)

- Any proposed future work is subject to change based on funding levels.

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Summary Slide

- X-ray microtomography used to generate surface meshes for simulation use
    - Novel sample holder used to image electrodes under realistic conditions
    - Found that solution wetting produced significant changes in thickness, has significant implications for models and experiments

- Transport properties measured by PFG-NMR
    - Determined degrees of ion-pairing
    - Properties corrected for ion pairing

- Salt diffusivity measured in microfluidic channel
    - Approximately in agreement with PFG-NMR analysis

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